

Speciation of Zn in a smelter-impacted soil

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INTRODUCTION

More than hundred years of ore-processing activities have severely impacted the natural environment, and specifically soils resulting in some heavy polluted areas losing the vegetation cover [1]. Determining the chemical form of toxic metals is of fundamental importance for assessing the chemical risk posed by their presence in agricultural fields, forest soils, and gardens, and developing effective remediation strategies in the most contaminated areas.

Micro-EXAFS and micro-SXRF were used to study the speciation and spatial distribution of Zn in a smelter-impacted soil located in the North of France in the vicinity of an ancient Zn, Pb, and H₂SO₄ plant. This plant was active during the first half of the 20th century, and was the third largest smelter in the world. Surrounding soils have been contaminated by Zn- and Pb-rich fly ashes originating from high-temperature smelting process and containing predominantly franklinite (ZnFe₂O₄), willemite (Zn₂SiO₄) and unidentified Pb compounds. Zn and Pb were progressively released in soil solutions during the weathering of slag materials, and dissolved species precipitated or were taken up by soil constituents. The profile concentrations of Zn and Pb with depth indicate that Zn is much more mobile than Pb: At about 110 cm depth, the Zn concentration still reaches 500 ppm as compared to a geochemical background of 70-100 ppm (Fig. 1). EXAFS and SXRF measurements were carried out on samples collected at 40-50 cm depth in order to assist us in the identification of Zn-precipitated and Zn-sorbed phases.

EXPERIMENT

Measurements were performed on the 10.3.2. station [2]. A polished 30 µm-thick soil section indurated in epoxy was rastered in 6 µm steps through the focused monochromatic X-ray beam, and the selected K α fluorescence was integrated for one second per point corresponding to a total data collection time of approximately 8 h. A typical energy dispersive fluorescence spectrum obtained after ~ 8 h is shown in Fig. 2. The total signal is heavily dominated by the Fe and Mn fluorescence-yield of the soil matrix and, in EXAFS spectroscopy, the desired Zn signal makes only ~ 2 10⁵ counts while typically 10⁶ good counts are suitable to get an acceptable precision of 10⁻³. In spite of this curse due to the present flux limitation on this station (~ 10⁸ ph/s/µm²), EXAFS spectra with an acceptable S/N ratio were successfully obtained by averaging 8-10 spectral sweeps of ~ 1 hour each thanks to the high stability of the spectrometer optics.

RESULTS AND DISCUSSION

Fig. 3 shows the spatial distribution of Mn, Fe, and Zn in a (Fe,Mn)-rich zone of the soil clay matrix. Highest Zn concentrations were encountered in Fe-rich grains, but Zn is also partly associated to Mn. Mn and Zn-µEXAFS spectra were collected in a Mn-rich zone, and a Fe-EXAFS spectrum was collected on a Fe-rich grain. Metal-bearing phases were identified from the comparison of EXAFS spectra with a large database of references. Fig. 4 shows that Fe grains have a δFeOOH-like structure and that the Mn rich concretion is made of a phyllomanganate, birnessite-like, compound. The Zn-EXAFS spectrum closely resembles the Zn-sorbed birnessite model compound in which Zn is bounded at layer vacancy sites [3] (Fig. 5). This experiment

demonstrates the potential of coupled μ SXRF and μ EXAFS measurements to directly determine metal species on a very small spatial scale in chemically and structurally heterogeneous natural systems.

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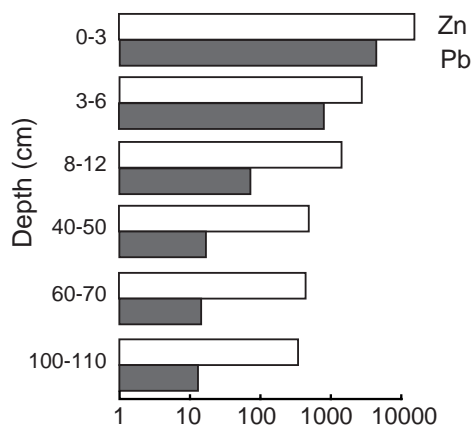


Fig. 1: Concentration of Zn and Pb in the $<100\ \mu\text{m}$ soil fraction (ppm).

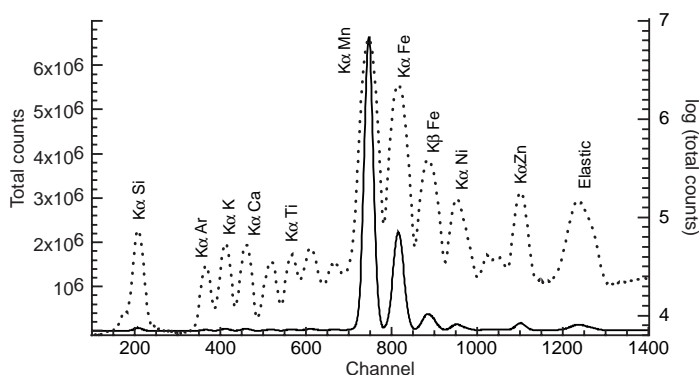


Fig. 2: X-ray fluorescence spectrum.

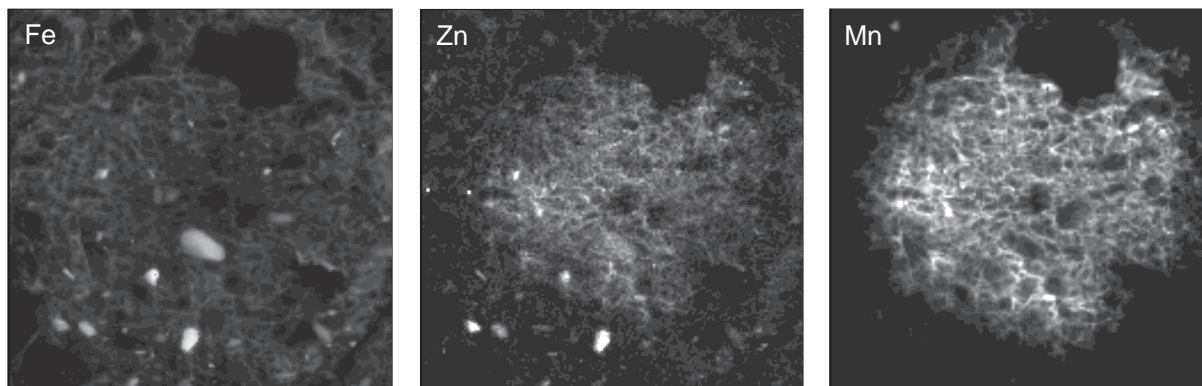


Fig. 3: Gray-scale map of the distribution of Fe, Mn, and Zn in the soil matrix. Zn is partly associated to Fe in Fe-rich grains and to Mn in the Mn-rich concretion. Size of the map: 1 x 1 mm.

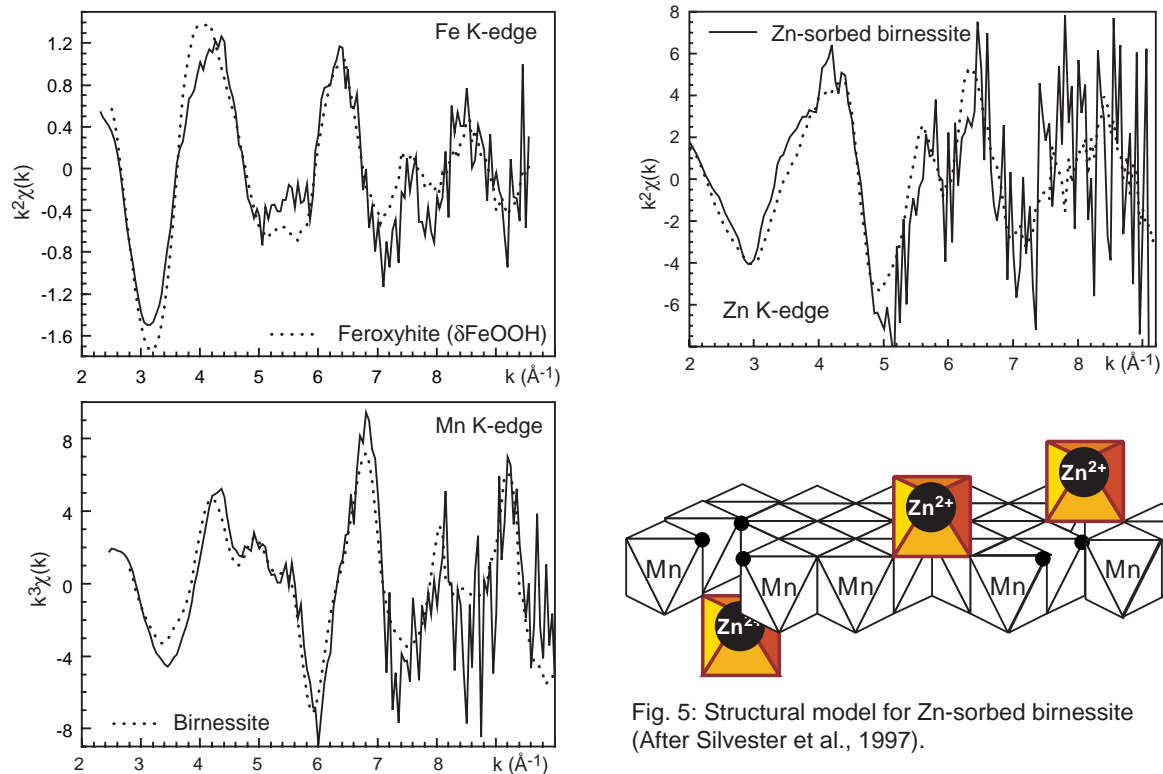


Fig. 4: micro-EXAFS measurements from the Mn- and Fe-rich regions. lines: exp. spectra; dots: reference spectra.

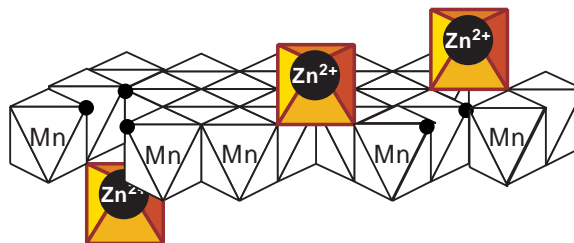


Fig. 5: Structural model for Zn-sorbed birnessite (After Silvester et al., 1997).

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